

Extraction chromatographic method of preconcentration and separation of lead(II) with high molecular mass liquid cation exchanger, Versatic 10

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A selective method has been developed for the extraction chromatographic separation of lead(II) with Versatic10 (liquid cation exchanger) coated on silanised silica gel. Its quantitative extraction has been achieved from 0.1M acetate buffer at the optimum pH 4.5-6.0. The effects of pH, flow-rate, stripping agents on extraction and elution have been investigated. Exchange capacity of the prepared exchanger at different temperatures with respect to lead(II) has been determined. The extraction equilibrium constant (K_{ex}) and different standard thermodynamic parameters have also been calculated by temperature variation method. The effect of pH on R_f values in ion exchange paper chromatography has been investigated. Lead(II) has been separated from synthetic multi-component mixtures containing various metal ions associated with it in ores and alloy samples. The method effectively permits sequential separation of lead(II) from synthetic quaternary mixture containing its congeners Cu(II), Sn(II), Hg(II) and Cu(II), Cd(II), Bi(III) of the same analytical group. The method is found effective for removal and recovery of lead(II) from industrial waste and standard alloy samples following its preconcentration on the column. A plausible mechanism for the extraction of lead(II) has been suggested.

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Lead is a toxic and relatively rare element (10^{-3} wt %), but it is well known because of its technical importance. It is an important constituent of some copper alloys and tin base white metals. Lead, in its trace level, appears to have deleterious effects on children's behavior and attentiveness, and possibly also on their IQs¹. It also decreases enzymatic and kidney functions and also causes neuromuscular difficulties². Obviously trace level separation of metallic toxicant lead(II) poses a challenging problem to the analytical chemists. The most widely used techniques for the separation and preconcentration of trace level lead(II) includes liquid-liquid extraction³, coprecipitation⁴⁻⁶, ion-exchange⁷, adsorption^{8,9}, cloud point extraction¹⁰, electrochemical deposition¹¹ and solid phase extraction (EC)¹²⁻¹⁴. But, except EC, all other techniques may be ineffective or extremely expensive, when the metals are in large volumes of relatively low concentrations¹⁵. EC is based on the utilization of a major constituent as the supporting phase with different coating materials¹⁶⁻¹⁸ such as polyelectrolyte, high molecular mass carboxylic acid (HMMCA), chelating agent, surfactant, high molecular mass amine (HMMA), etc. The essential requirements of sorbents in EC are: (1) the possibility to extract selectively a large number of analytes over

a wide pH range, (2) quantitative sorption and elution ability, (3) kinetically faster sorption and desorption mechanism, (4) high retention capacity, (5) regenerability, (6) accessibility, and, (7) mechanical and chemical stability¹⁹. There are several reports on HMMCA and HMMA on hydrophobic silica support for selective separation of metal ions^{17,20-24}. Silica gel is found to act as a successful support since it does not swell or strain, has good mechanical strength and can undergo heat treatment²⁵. In our laboratory, SRS-100 on hydrophobic silica support has been effectively used for the extraction and separation of lead(II)²². But the systematic extraction chromatographic investigation of lead(II) with HMMCA, Versatic 10, has yet not been reported. Versatic 10, is a mixture of C₁₀ isomeric tertiary monocarboxylic acids, had the concentration and purity of 5.2 M and 99% respectively²⁶, and it is soluble in several solvents like benzene, toluene, *n*-hexane, xylene, butanol, carbon tetrachloride, chloroform, nitrobenzene and diisopropyl ether^{26,27}. It has a good thermal and chemical stability²⁶ and efficiently extracts metal ions from aqueous solution over a wide range of pH²⁷⁻²⁹. The present work reports a rapid method for the extraction and preconcentration of microgram level lead(II) with HMMCA, Versatic 10, on hydrophobic silica support.

Materials and Methods

Digital Elico L1-120 pH meter combined with glass electrode; a 7D-1F thermostat, spectrophotometer (Beckmann DU-6 ECIL GS 5700A); Shimadzu FTIR spectrophotometer (model no FTIR -8400S), Perkin-Elmer atomic absorption spectrophotometer (model no. Analyst 400), equipped with a standard burner with an air-acetylene flame, a standard hollow cathode lamp as the line source and chromatographic glass column (0.8×8 cm.) with glass-wool plug at the bottom were used in the present study.

The liquid cation exchanger, Versatic 10 (Shell Chemical, London), a mixture of high molecular mass C₁₀ isomeric tertiary monocarboxylic acid, was used without any further purification. Dimethyldichlorosilane was used to make the silica gel (120 mesh) hydrophobic. A standard stock solution of lead(II) (3.02 mg mL⁻¹) was prepared by dissolving Pb(NO₃)₂ (AR) in water and estimated complexometrically with EDTA using xylenol orange as indicator. The solution containing 30.2 µg mL⁻¹ of lead(II) was prepared through appropriate dilution. Buffer solutions of different pHs were prepared from acetic acid (0.1 M) and ammonium acetate (0.1 M) in proper ratio. Lower pH values were adjusted with help of 0.2M chloroacetic acid. All chemicals and solvents used in this work, unless otherwise stated, were of analytical grade (BDH/Merck).

Preparation of ion exchange material

Silica gel (120 mesh) was rendered hydrophobic by exposing it to vapour of dimethyldichlorosilane (DMDCS) in N₂ atmosphere. The DMDCS treated (silanised) silica gel was then washed with anhydrous methanol and dried at 100°C. The silanised silica gel was impregnated with Versatic10, diluted in benzene and was dried in a rotary vacuum evaporator to achieve uniform coating. Excess benzene was removed by washing the exchanger with 2 M HCl. Each column could be used for at least 30 cycles without any loss of its exchange capacity. For ion exchange paper chromatography, 0.5 ml Versatic 10 was taken in 20 ml benzene and paper strip (Whatman No 1) was immersed in it and dried in air. Lead(II) solution (in µg) was taken on the paper strip containing exchanger and developed with acetate buffer (pH~5.5): acetone (25:1 v/v) as the developing solvent.

Exchange capacity and breakthrough capacity

The exchange capacity of the prepared exchanger was determined at different temperatures by

measuring the miliequivalent (meq.) of sodium ions absorbed by 1 g of dry exchanger in H⁺ form. The exchange capacity was found to be 2.44 meq. of H⁺ g⁻¹ of dry exchanger at 25° and which is comparable to the literature value²¹. The pHs of the exchanger bed and lead(II) solution (0.2 mg mL⁻¹) was adjusted to the desired value with acetate buffer (0.1 M) and then the lead(II) solution was passed through the column containing 1 g of dry exchanger. It was found that the leakage of lead(II) started at pH 5.5 and 5.75 after passing 105 mL (21 mg) and 125 mL (25 mg) of effluent respectively and so the uptake of lead(II) increases with the increase in pH. After its extraction, Pb(II) was eluted with 20 mL 0.01 M HNO₃. Thus the preconcentration of 5.25 and 6.25 times on milligram level were achieved in the column.

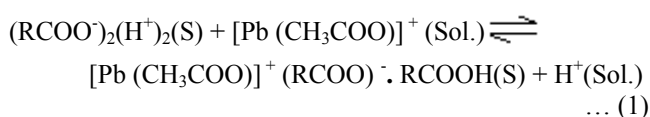
General extraction

The ion exchanger was loaded in the chromatographic column (id: 0.8 cm) and the pH of the exchanger bed was adjusted to the desired value with acetate buffer solution (0.1 M). An aliquot containing 30.2 µg of lead(II) in acetate buffer was passed through the column (pre-adjusted pH 5.5), at a flow rate of 1.0 mL min⁻¹. After extraction, lead(II) was stripped with 0.01 M HNO₃. A number of fractions were collected and the amount of lead(II) from each fraction was determined spectrophotometrically using Arsenazo III as chromogenic reagent at 605 nm.

Results and Discussion

The systematic extraction chromatographic studies on lead(II) with Versatic 10 at the pH range 3.0-6.5 ensured its quantitative extraction at the optimum pH range of 4.5-6.0. The complete retention of lead(II) at the column was found even at a flow rate of 2.5 mL min⁻¹. Common anions like Cl⁻, SO₄²⁻, ClO₄⁻, NO₃⁻ and cations like Ca(II), Mg(II), Co(II), Ni(II), Zn(II), Sn(II), and Cd(II) did not interfere in the extraction of lead(II). FTIR spectra of the exchanger containing -COOH group shows a strong absorption at 1720.8 cm⁻¹. However, the position of the peak is shifted to lower range (1664.6 cm⁻¹) in the spectra of Pb(NO₃)₂ loaded exchanger. This decreasing of stretching frequency indicates the conversion of -COOH group to -COO⁻ ion. The tetramer, [Pb₄(CH₃COO)₄]⁺⁴ is present at higher acetic acid concentration (pH < 4.5) while the monomer, [Pb(CH₃COO)]⁺ is the predominant species at lower acetic acid level (pH > 4.5). At pH 5.1, plot of log D against log C_[CH₃COO-] gives a linear relationship

($y = 0.9833x + 1.5816$; $R^2 = 0.9812$) with slope of 0.98 at fixed concentration of extractant and fixed concentration of Pb(II). While, a linear relationship ($y = 1.873x + 2.7778$; $R^2 = 0.9712$) is obtained with slope = 1.9 between $\log D$ and $\log C_{[\text{Versatic } 10]}$ at pH 5.1, fixed concentration of acetate and fixed concentration of lead(II). At pH 4.5-6.5, Versatic 10 exists as a dimer in organic solvent. Hence, the probable composition of the extracted species is 1:2:1 (metal:extractant:acetate). Bearing this in mind, it has been suggested that Pb(II) first produces the monomer, $[\text{Pb}(\text{CH}_3\text{COO})]^+$ with acetate ion at pH 4.5-6.5 and having suitable size and charge, this monomer goes to the exchange site as per following proposed path:



At higher pH (>6.0), lead(II) hydrolyzed and did not participate in the exchange process.

The extraction equilibrium constant (K_{ex}) was computed at different temperatures using Eq. (2)³⁷. A linear plot of $\log K_{\text{ex}}$ against $1000/T$ was obtained.

$$K_{\text{ex}} = [\text{H}^+] E_{\text{R}} / [(\text{RCOO}^-)_2(\text{H}^+)_2(\text{S})] \quad \dots (2)$$

where $[(\text{RCOO}^-)_2(\text{H}^+)_2(\text{S})]$ denotes the concentration of Versatic 10 and E_{R} is the ratio of extracted metal ion to its unextracted portion.

The effect of temperature on extraction of lead(II) has been made for the determination³⁰ of different thermodynamic parameters at pH 5.5 using the standard van't Hoff equation. The enthalpy change (ΔH) was evaluated from the plot of $\log K_{\text{ex}}$ versus $1000/T$. The free energy change (ΔG) and entropy change (ΔS) at room temperature (298 K) were also calculated. The positive value of ΔH (0.04 kJ mol⁻¹) and smaller ΔS (0.01 kJ mol⁻¹) rationalizes the endothermic nature of the extraction process. The lower negative value of ΔG (-2.95 kJ mol⁻¹) suggests the spontaneity and reversibility of the equilibrium.

Stripping agents

After extraction, to select the specific stripping agents, lead(II) was stripped with demineralised water and various acids of different concentrations. The systematic studies on stripping behavior gave the quantitative elution of lead(II) with HNO₃ with concentration > 0.001M, HCl with concentration > 0.003M and CH₃COOH with concentration > 0.005M. It was found that 0.01M HNO₃ gave the

best stripping (least required volume 20 mL), hence it was used as stripping agent in all further experiments. The elution process (back extraction) follows the reverse reaction of extraction (Eq. 1) and Pb(II) is eluted with H⁺ as tetramer. The minimum required acid concentration of HNO₃ and HCl are lower than that of CH₃COOH. Acetic acid (organic acid) is poorly dissociated in aqueous solution and quantitative elution of lead(II) occurs with comparatively higher concentration. Low level of the mineral acids elute lead(II) from the exchanger bed through the formation of nitro, $\text{Pb}(\text{NO}_3)^+$ and corresponding chloro cations.

Ion exchange paper chromatography

At pH 5.5, the R_f values were determined in acetate buffer-acetone mixture (25:1 v/v) on chromatogram. Results show that under this recommended condition Sn(II), Zn(II), Mg(II), Ca(II), Cr(III), Cd(II) are very weakly bound (R_f values ~0.9), metal ions like Al(III), Pb(II), Cu(II), Ga(III), Bi(III) are moderately bound (R_f values 0.3-0.5), while Tl(III) is tightly bound with the stationary phase (R_f values ~0.08). At pH 2.5 binding strength of Zr(IV) is much higher than that of Fe(III). At ~pH 5.5, Sn(II) exists as an anionic complex, $[\text{Sn}(\text{CH}_3\text{COO})_3]^-$ and moves at a fastest rate with the mobile phase. With acetate ion the complexity constant for Ca(II) is much higher than that for Mg(II). So Ca(II) moves at a faster rate than Mg(II). $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ is acidic and the constants K_A for Cr(III), Al(III), Ga(III), In(III) and Tl(III) respectively, are 10^{-4} , 10^{-5} , 10^{-3} , 10^{-4} and 10^{-1} . $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ protonates the acetate ion quickly and the conjugate base $[\text{M}(\text{OH})(\text{H}_2\text{O})_6]^{2+}$ is produced with the formation order as: $[\text{Tl}(\text{OH})(\text{H}_2\text{O})_6]^{2+} \gg [\text{Ga}(\text{OH})(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{OH})(\text{H}_2\text{O})_6]^{2+} > [\text{Al}(\text{OH})(\text{H}_2\text{O})_6]^{2+}$. It is suggested that the most easily formed mono hydroxo species, $[\text{Tl}(\text{OH})(\text{H}_2\text{O})_6]^{2+}$ binds preferably with the exchange site. As a result its movement in the mobile phase is retarded. $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Al}(\text{OH})(\text{H}_2\text{O})_6]^{2+}$ with the lowest formation tendency move at the fastest rate. Aqua ions of Zn(II), Cd(II), Hg(II) are quite acidic and the corresponding hydroxo species, $[\text{M}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ are produced and equilibrated during the development of chromatogram. The increasing affinity order is directly related to decreasing order of their hydrated radii.

Separation of lead(II) from multicomponent synthetic mixtures

In order to assess the possible analytical applications the proposed method was applied to separate lead(II) from multicomponent synthetic mixtures containing

lead(II) with different metal ions commonly associated with it in same analytical group, ores and alloy samples (Table 1). After recovery, diverse metal ions were determined complexometrically and lead(II) was estimated spectrophotometrically. Separation of lead(II) from diverse metal ions in binary and multi-component synthetic mixtures follows the R_f values and Kielland principle, 'affinity order of the cations for cation-exchange resin is approximately the order of their hydrated ionic radii (inverse of the order of their radii).

Prior to column experiments, ion exchange paper chromatography was carried out in acetate buffer of varying pHs and best resolution of ions was found with respect R_f values at $pH \sim 5.5$ in the

chromatogram. Synthetic mixture containing lead(II), copper(II), tin(II) and bismuth(III) were passed through the column at $pH 5.5$. Under this condition except tin(II), all other metal ions were extracted at the column. Sn(II) passed through the column as carboxylato anion complex, $[Sn(CH_3COO)_3]^-$. Under the present conditions, copper(II) and mercury(II) are present as hydroxo cation, $[Cu(OH)(H_2O)]^+$ and $[Hg(OH)(H_2O)]^+$. The larger sized mercuric cation (smaller hydrated radii) goes to the exchanger site with higher affinity. Lead was eluted first with $0.005M CH_3COOH$, followed by the sequential elution of copper(II) and mercury(II) has been made with $0.05 M CH_3COOH$ and $1M HCl$ respectively. When equilibrated with the exchanger at $pH 5.5$, in

Table 1—Separation of lead(II) from multicomponent synthetic mixtures. [Col. = 0.8×8 cm.; flow-rate = 1.0 ml min^{-1} ; $pH = 5.5$]

Metal ions	Weight of the metal ions (μg)		Recovery (%)	Rel. error (%)	Eluents used	Vol. of eluent (mL)
	Added	Recovered ^a				
Fe(III) ^b	2874	2908	101.18	1.16	$0.5M H_2SO_4$	50
Co(II)	3866	3843	99.40	-0.60	-	30
Pb(II)	30.20	30.40	100.66	0.66	$0.01M HNO_3$	20
Tl(III)	3000	3049	101.63	1.61	$0.05M HCl$	20
Fe(III) ^b	2874	2910	101.25	1.24	$0.5M H_2SO_4$	50
Ni(II)	4200	4196	99.91	-0.10	-	30
Pb(II)	30.20	30.38	100.6	0.59	$0.01M HNO_3$	20
Tl(III)	3000	2978	99.28	-0.74	$0.05M HCl$	20
Fe(III) ^b	2874	2906	101.1	1.10	$0.5M H_2SO_4$	50
Cd(II)	3040	3002	98.75	-1.27	-	30
Pb(II)	30.20	30.62	101.39	1.37	$0.01M HNO_3$	20
Tl(III)	3000	2962	98.73	-1.28	$0.05M HCl$	20
Fe(III) ^b	2874	2916	101.46	1.44	$0.5M H_2SO_4$	50
Zn(II)	3260	3222	98.83	-1.18	-	30
Pb(II)	30.20	30.68	101.59	-1.57	$0.005M HNO_3$	50
Hg(II)	2724	2696	98.97	-1.04	$0.1M HNO_3$	30
Fe(III) ^b	2874	2900	100.9	0.89	$0.5M H_2SO_4$	50
Cd(II)	3040	3008	98.95	-1.06	-	30
Pb(II)	30.20	30.56	101.19	1.18	$0.005M HNO_3$	50
Hg(II)	2724	2688	98.68	-1.34	$0.1M HNO_3$	30
Fe(III) ^b	2874	2902	100.97	0.97	$0.5M H_2SO_4$	50
Cr(III)	2528	2506	99.13	0.88	-	30
Pb(II)	30.20	30.42	100.73	0.72	$0.005M HNO_3$	50
Hg(II)	2724	2692	98.82	-1.19	$0.1M HNO_3$	30
Sn(II)	2874	2912	101.32	1.30	-	50
Pb(II)	30.20	30.04	99.47	-0.60	$0.005M CH_3COOH$	80
Cu(II)	2734	2762	101.1	1.02	$0.05M CH_3COOH$	20
Hg(II)	3000	2966	98.87	-1.15	$1 M HCl$	20
Cd(II)	3260	3288	100.86	0.85	-	30
Pb(II)	30.20	30.02	99.40	-0.60	$0.005M CH_3COOH$	80
Cu(II)	2724	2764	101.47	1.44	$0.05M CH_3COOH$	20
Bi(III)	3000	2978	99.27	-0.74	$1 M HCl$	20

^aAverage of five determinations; standard deviation < 0.07

^b $pH = 2.5$

Table 2—Preconcentration, removal, recovery of Pb(II) and Cu(II) / Sn(II) from industrial and alloy samples

Samples (comp.)	Pb(II) (%)		Sn(II) ^a or Cu(II) ^b (%)	
	Found ^c	Recovery	Found ^c	Recovery
Solder(11g) Pb(II)=40% Sn(II)=59.9%	37.2 (s.d.= 0.35) (P.F. = 46.5)	93.0	54.8 ^a (s.d.= 0.38)	91.48 ^a
Lead conc.(42G)/ Pb(II)=75.6% Cu(II)=0.14%	71.26 (s.d.=0.39) (P.F. = 47.1)	94.26	0.12 ^b (s.d.= 0.36) (P.F.= 42.8)	85.71 ^b
Brass 5g Pb(II)=2.23(%) Cu(II)=67.4(%)	2.12 (s.d.=0.41) (P.F. = 47.5)	95.07	63.04 ^b (s.d.= 0.37) (P.F. = 46.7)	93.53 ^b
Electroplating waste Pb(II)=11.2(mg dm ⁻³) Cu(II)=10.0(mg dm ⁻³)	10.1 (s.d.= 0.38) (P.F. = 45.1)	90.18	9.40 ^b (s.d.= 0.33) (P.F. = 47)	94.0 ^b

^aSn(II); ^bCu(II); ^cAverage of five determinations

the synthetic mixture containing lead(II), copper(II), cadmium(II) and bismuth(III), except cadmium(II), all other metal ions were quantitatively extracted at the column. Lead was eluted first with 0.005M CH₃COOH, and then the subsequent sequential elution of copper(II) and bismuth(III) was carried out with 0.05 M CH₃COOH and 1M HCl respectively (Table 1).

For all other quaternary synthetic mixtures metal ions are separated by a two-step extraction process. At pH 2.5 only Fe(III) was extracted while other three ions percolated through the column. The effluent containing the three unextracted ions was again equilibrated with the exchanger at pH 5.5 and separated from each other with selective eluents.

Application to real samples

The effectiveness of the proposed method was judged by separating lead(II) from some standard alloy samples. The feasibility of the process was tested with the effluent obtained from a typical electroplating industry. High degree of preconcentration (1000ml to 20 ml) (~50-fold) with subsequent removal, or recovery (> 90%) of lead(II) and the associated metals with low standard deviation (< 0.38) for industrial samples were obtained. After removal, recovery of lead(II) and other metal ions from effluent and alloy samples were determined by AAS (Table 2). Wet digestion of the samples with mineral acids was made prior to determining metal ions by AAS following the standard procedure³¹.

The proposed method is simple, rapid and selective and needs only 2.5 hours for separation and estimation of lead(II). Clean separation of lead(II) has been achieved from several toxic and heavy metal ions like copper(II), iron(III), chromium(III), zinc(II), cadmium(II), mercury(II), thallium(III), zirconium(IV), lanthanum(III), and thorium(IV). The separation of lead(II) from these toxic and heavy metals has great importance to the environmental and analytical chemist. Lead(II) has been successfully separated from its congeners copper(II), tin(II), cadmium(II) and bismuth(III) of the same analytical group. In all the cases the metal ions were determined complexometrically. The method was found selective at the optimized conditions for lead(II) and does not need separation of other constituents present in the matrix. Very small amount (~0.2 mL) of liquid extractant in the developed exchanger can selectively separate lead(II) from these wide variety of multi-component mixtures containing large number of heavy, toxic and conger cations. The developed exchanger is chemically stable (in 6M HNO₃, 4M CH₃COOH, 4M HCl and 2M H₂SO₄) and effective over a wide range of pH. It can be used for more than 30-40 cycles without any loss its exchange capacity. These show its additional advantages over the other conventional exchangers¹²⁻¹⁸. Results achieved in all this experiments are satisfactory, recoveries quantitative (> 99%), with standard deviation < 0.07 and the relative error within ± 1.5%. The removal and preconcentration data for lead(II) for a typical electroplating waste were found 90.18 and 45.1, respectively with a standard deviation of 0.38; while that for Cu (II) are 94, 47 and 0.33 respectively.

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